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PATENT ABSTRACTS OF JAPAN

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(54) ADDITIVE FOR PAPER MAKING

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an additive for paper making having excellent drainage effect by copolymerizing an acrylamide with an anionic and a cationic vinyl monomers and N,N'-bis[(meth)acrylamidoalkylene]urea.

SOLUTION: This additive for paper making comprises 10-30 wt.% solid content concentration of a copolymer obtained by copolymerizing 97.995-55 mol% of an acrylamide such as (meth)acrylamide with 1-20 mol% of an anionic vinyl monomer selected from itaconic acid, acrylic acid or its salt, 1-20 wt.% of a cationic monomer such as 2-hydroxy-N,N,N,N',N'-pentamethyl-N'-[3{1-oxo-2-propenyl}amino]propyl]-1,3-propenediaminium chloride and 0.005-5 wt.% of N,N'-bis[(meth)acrylamidoalkylene]urea.

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CLAIMS

[Claim(s)]

[Claim 1] (a) The additive for paper manufacture characterized by containing the copolymer obtained by carrying out the polymerization of the acrylamide, (b) anionic vinyl monomer, (c) cationic vinyl monomer and (d) N, and N'-bis(meta) (acrylamide alkylene) ureas.

[Claim 2] Said additive for paper manufacture according to claim 1 characterized by said copolymer being a copolymer which comes to carry out the polymerization of the (d) N and N'-bis(meta) (acrylamide alkylene) ureas 0.005 - five-mol % (c) cationic vinyl monomer 1 - 20-mol% (b) anionic vinyl monomer 1 - 20-mol% (a) acrylamide 97.995 - 55-mol%.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the additive for paper manufacture which is excellent in the filterability effectiveness in more detail about the additive for paper manufacture.

[0002]

[Description of the Prior Art] For the purpose of energy saving and the deployment of a resource to that set like the paper maker conventionally and use of a virgin pulp was restricted with aggravation of a bolt supply situation, and a pan Closed **** of Hokusui increases by that the need for reuse of used paper became strong further, wastewater regulation, etc., and the various additives for paper manufacture are used for that the amount of the impurity contained all over Hokusui increased, and the improvement in the productivity accompanying improvement in the speed of a paper machine or upgrading of paper.

[0003] Although the acrylamide system polymer which uses starch, polyamide polyamine-epichlorohydrin resin, melamine formaldehyde resin, formaldehyde resin, and acrylamide as a principal component as a paper durability agent and a filtration improvement agent among the additives for paper manufacture is used according to the purpose, generally the acrylamide system polymer is most widely used especially from the ease of dealing with it on the advantage on the composition, the engine performance, and use.

[0004] As an additive for paper manufacture which consists of an acrylamide system polymer, the anion type, the cation type, and the both-sexes type are known by the ionicity.

[0005] As an anion type, there are a copolymer with these monomers and the nonionic vinyl monomer which may be copolymerized, a partial hydrolysate of an acrylamide system polymer, etc. the vinyl monomer (an "anionic vinyl monomer" can also be called.) which has acrylamides and an anion radical, and if needed. As a cation type, there is a copolymer with these monomers and the nonionic vinyl monomer which may be copolymerized, the Hoffmann denaturation object or a MANNIHHI denaturation object of an acrylamide system polymer, etc. the vinyl monomer (a "cationic vinyl monomer" can also be called.) which has acrylamides and a cation radical, and if needed. As a both-sexes type, there is the Hoffmann denaturation object or a MANNIHHI denaturation object of a copolymer with acrylamides, the vinyl monomer which has a cation radical, the vinyl monomer which has an anion radical, and the vinyl monomer which has a copolymer, acrylamides, and an anion radical with these monomers and the nonionic vinyl monomer which may be copolymerized if needed etc.

[0006] However, in the paper manufacture industry in recent years, factors, such as aggravation of the above raw material situations of paper, increase of the amount of impurity in Hokusui which produces a paper maker in inside, and fluctuation of paper making pH, have been increasing. The present condition is that effectiveness sufficient with the well-known additive for paper manufacture until now is not acquired to these factors.

[0007] Therefore, branching structure is given to an acrylamide system polymer, and in order to make molecular weight increase, various polyfunctional vinyl monomers are used. It replaces with the acrylamide system polymer before giving branching structure and making molecular weight increase,

and if the acrylamide system polymer of the amount of macromolecules which gave branching structure using the polyfunctional vinyl monomer is adopted as an additive for paper manufacture, it is thought that it is effective in paper durability and filterability improving. It is thought by this effectiveness's giving branching structure and making molecular weight increase that it originates in the contact of an acrylamide system polymer and pulp having increased, the cellulose intermolecular hydrogen bridge in pulp having increased, and condensation of pulp having become strong etc.

[0008] However, while condensation of too much pulp raises filterability, it worsens the conditions of perfect paper and causes the problem of reducing paper durability.

[0009]

[Problem(s) to be Solved by the Invention] This invention makes it a technical problem to offer the new additive for paper manufacture which can give the filterability and yield nature which were excellent while maintaining the paper durability which is not inferior to them compared with additives for paper manufacture which are known from the former, and which gave branching structure using the additives for paper manufacture and well-known polyfunctional vinyl monomers, such as a polyacrylamide system polymer with low molecular weight, relatively, such as an acrylamide system polymer of the amount of macromolecules.

[0010]

[Means for Solving the Problem] In order that this invention person may solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, it differs from additives for paper manufacture, such as an acrylamide system polymer which carried out macromolecule quantification using the well-known polyfunctional vinyl monomer. New specific N and the N'-bis(meta) (acrylamide alkylene) urea which lengthened distance between polymerization nature double bonds, using a urea as a SU **-sir A header, It succeeded in giving the filterability and yield nature which were excellent while maintaining paper durability equivalent to them compared with the conventional additive for paper manufacture by using this N and an N'-bis(meta) (acrylamide alkylene) urea for the additive for paper manufacture.

[0011] The 1st means for solving said technical problem (a) acrylamides (b) An anionic vinyl monomer, (c) cationic vinyl monomer, And it is the additive for paper manufacture characterized by consisting of a copolymer obtained by carrying out the polymerization of the (d) N and N'-bis(meta) (acrylamide alkylene) ureas. In the suitable mode in said 1st means Said copolymer (a) acrylamide 97.995 - 55-mol %, (b) It is the polymer which comes to carry out the polymerization of the (c) cationic vinyl monomer 1 - 20-mol % and (d) N, and N'-bis(meta) (acrylamide alkylene) ureas 0.005 - five-mol % anionic vinyl monomer 1 - 20-mol%.

[0012]

[Embodiment of the Invention] The additive for paper manufacture of this invention consists of a copolymer obtained by carrying out the polymerization of the (a) acrylamide, (b) anionic vinyl monomer, (c) cationic vinyl monomer and (d) N, and N'-bis(meta) (acrylamide alkylene) ureas.

[0013] - As acrylamides ("a component" may be called) in (a) acrylamide-this invention Besides acrylamide and methacrylamide, for example, N-methyl (meta) acrylamide, N-ethyl (meta) acrylamide, N, and N-dimethyl (meta) acrylamide, N permutation (meta) acrylamides, such as N and N-diethyl (meta) acrylamide, N-isopropyl (meta) acrylamide, and N-t-octyl (meta) acrylamide, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together. These desirable are acrylamides (meta).

[0014] - As an anionic vinyl monomer ("b component" may be called) in (b) anionic vinyl monomer-this invention A carboxyl group content vinyl monomer, a sulfonic group content vinyl monomer, a phosphonic acid radical (- PO₂ (OH)) content vinyl monomer, etc. can be mentioned. For example, as said carboxyl group content vinyl monomer Partial saturation monocarboxylic acid, partial saturation dicarboxylic acid, partial saturation tricarboxylic acid, And those salts, such as partial saturation tetracarboxylic acid, etc. can be mentioned. Those salts, such as a partial saturation sulfonic acid, etc. can be mentioned as said sulfonic group content vinyl monomer. Those salts, such as partial saturation phosphonic acid, etc. can be mentioned to a list as said phosphonic acid radical content vinyl monomer,

and these may be used by the one-sort independent and may use two or more sorts together.

[0015] As said partial saturation monocarboxylic acid, an acrylic acid, a methacrylic acid, etc. can be mentioned and alkali-metal salts, such as sodium salt of unsaturated carboxylic acid and potassium salt, ammonium salt, etc. can be mentioned as salts of said partial saturation monocarboxylic acid.

[0016] A maleic acid, a fumaric acid, an itaconic acid, a citraconic acid, etc. can be mentioned, and alkali-metal salts, such as sodium salt of partial saturation dicarboxylic acid and potassium salt, ammonium salt, etc. can specifically as said partial saturation dicarboxylic acid be mentioned specifically as salts of said partial saturation dicarboxylic acid.

[0017] They are specifically as said partial saturation tricarboxylic acid aconitic acid, 3-butene-1, 2, 3-tricarboxylic acid, and 4-pentene. - 1, 2, and 4-tricarboxylic acid etc. can be mentioned and alkali-metal salts, such as sodium salt of partial saturation tricarboxylic acid and potassium salt, ammonium salt, etc. can specifically as salts of said partial saturation tricarboxylic acid be mentioned.

[0018] It is specifically as said partial saturation tetracarboxylic acid 1-pentene. - They are 1, 1, 4, and 4-tetracarboxylic acid and 4-pentene. - They are 1, 2, 3, 4-tetracarboxylic acid, and 3-hexene. - 1, 1, 6, and 6-tetracarboxylic acid etc. can be mentioned, and alkali-metal salts, such as sodium salt of partial saturation tetracarboxylic acid and potassium salt, ammonium salt, etc. can specifically as salts of said partial saturation tetracarboxylic acid be mentioned.

[0019] A vinyl sulfonic acid, a styrene sulfonic acid, an allyl compound sulfonic acid, 2-acrylamido-2-methyl propane sulfonic acid, etc. can be mentioned, and alkali-metal salts, such as sodium salt of a partial saturation sulfonic acid and potassium salt, ammonium salt, etc. can specifically as said partial saturation sulfonic acid be mentioned specifically as salts of said partial saturation sulfonic acid.

[0020] Vinyl phosphonic acid, alpha-phenyl vinyl phosphonic acid, etc. can be mentioned, and alkali-metal salts, such as sodium salt of said partial saturation phosphonic acid and potassium salt, ammonium salt, etc. can specifically as said partial saturation phosphonic acid be mentioned specifically as salts of said partial saturation phosphonic acid.

[0021] as said anionic vinyl monomer -- quality of paper -- considering points, such as the improvement effectiveness and economical efficiency, a kind is chosen from the group which is chosen from the group which consists of partial saturation monocarboxylic acid, partial saturation dicarboxylic acid, and these salts and which is desirable and consists especially of an itaconic acid, acrylic acids, and those salts at least -- especially a kind is desirable at least.

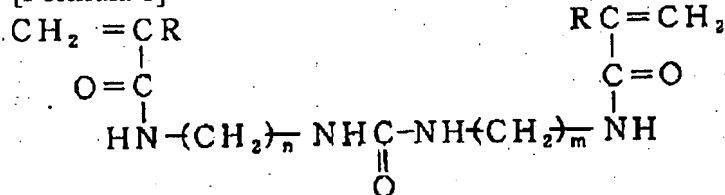
[0022] - (c) cationic vinyl monomer - as said cationic vinyl monomer ("c) component" may be called) For example, dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, Dimethylaminopropyl (meta) acrylate, diethylamino propyl (meta) acrylate, etc., The dialkylamino alkyl (meta) acrylate which is ester of dialkylamino alkyl alcohol and an acrylic acid (meta) Dimethylaminopropyl (meta) acrylamide, diethylamino propyl (meta) acrylamide, etc., Dialkylamino alkyl (meta) acrylamides and an alkyl diaryl amine, Amino-group content vinyl monomers including allylamines, such as dialkyl allylamine, a diaryl amine, and allylamine, ("the 3rd class amino-group content vinyl monomer, the 2nd class amino-group content vinyl monomer, and the 1st class amino-group content vinyl monomer" can also be called.) The salts of inorganic acids, such as a hydrochloric acid of said amino-group content vinyl monomer, a sulfuric acid, a formic acid, and an acetic acid, or an organic acid, Alkyl halide, such as said the 3rd class amino-group content vinyl monomer and methyl chloride, and a methyl bromide, Alkyl halide, such as benzyl chloride and a benzyl star's picture, A dimethyl sulfate, a diethyl sulfate, epichlorohydrin, 3-chloro-2-hydroxypropyl trimethylammoniumchloride, The vinyl monomer containing the quarternary ammonium salt obtained by the reaction with the 4th class-ized agents, such as glycidyl trialkyl ammonium chloride, For example, 2-hydroxy N, N and N, N', N'-pentamethyl-N'-[3-((1-oxo--2-propenyl) amino} propyl]-1, and 3-pro pansy aminium dichloride etc. can be mentioned. These may be used by the one-sort independent and may use two or more sorts together.

[0023] - (d) N and N'-bis(meta) (acrylamide alkylene) ureas - Said N and N'-bis(meta) (acrylamide alkylene) ureas ("d) component" may be called) can be shown as follows, and a - bis(acrylamide methylene) urea, and N'N, N'-bis(methacrylamide methylene) urea etc. can be suitably used for them in

this invention, for example. [N, and]

[0024]

[Formula 1]

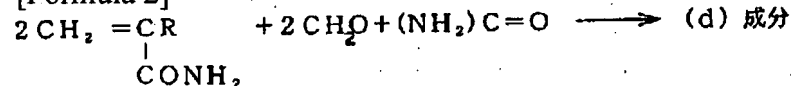


However, R shows a hydrogen atom or a low-grade alkyl group, for example, a methyl group, and an ethyl group among a formula, and m and n show the integer of 1-5, respectively.

[0025] Said N and an N'-bis(meta) (acrylamide methylene) urea can be obtained by the reaction shown below.

[0026]

[Formula 2]



However, R shows a hydrogen atom or a methyl group among a formula.

[0027] - others -- monomer component - it is also still more possible to introduce (e) nonionic vinyl monomer of these other than the above-mentioned configuration monomer and copolymerizable arbitration by request.

[0028] As said nonionic vinyl monomer ("(e) component" may be called), the ester of alcohol and an acrylic acid (meta), acrylonitrile (meta), styrene, a styrene derivative, vinyl acetate, propionic-acid vinyl, the methyl vinyl ether, etc. can be mentioned, for example, and these may be used by the one-sort independent and may use two or more sorts together.

[0029] In addition, in case the copolymer in this invention is manufactured, even if it uses together (f) polyfunctional monomer ("(f) component" may be called) in addition to the above (a) - (e) component, it does not interfere.

[0030] As the aforementioned (f) component, 2 functionality vinyl monomers, such as di(meth)acrylate, bis(meta) acrylamides, and divinyl ester, epoxy acrylate, urethane acrylate, 3 functionality vinyl monomer, 4 functionality vinyl monomer, a water-soluble aziridinyl compound, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0031] As the aforementioned (f) component, otherwise, a water-soluble polyfunctional epoxy compound, a silicon system compound, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together.

[0032] As said di(meth)acrylate, ethylene glycol di(metha)acrylate, diethylene GURIKORUJI (meta) acrylate, triethylene glycol di(metha)acrylate, propyleneglycol di(meth) acrylate, GURISERINJI (meta) acrylate, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0033] As said bis(meta) acrylamides, - screw acrylamide acetic-acid, and N'N, N'-screw acrylamide methyl-acetate, N, and N-benzylidene screw acrylamide etc. can be mentioned, for example, and these may be used by the one-sort independent and may use two or more sorts together. [methylenebis (meta) acrylamide, ethylene bis(meta) acrylamide, hexa methylenebis (meta) acrylamide, N, and]

[0034] As said divinyl ester, an adipic-acid divinyl, a sebacic-acid divinyl, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0035] As a polyfunctional vinyl monomer except said, allyl compound (meta) acrylate, diallyl phthalate, diallyl maleate, diaryl succinate, diaryl acrylamide, divinylbenzene, diisopropenylbenzene, N,

and N-diaryl methacrylamide, N-methylol acrylamide, diaryl dimethylammonium, diallyl chlorendate, glycidyl (meta) acrylate, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0036] As said 3 functionality vinyl monomer, 1, 3, 5-thioria chestnut roil hexahydro-S-triazine, triallyl isocyanurate, N, and N-diaryl acrylamide, a triaryl amine, triallyl trimellitate, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0037] as said 4 functionality vinyl monomer -- for example, tetramethylolmethane tetraacrylate, tetra-allyl compound pyromellitate, N and N, N', and N' - tetra-allyl compound-1,4-diaminobutane, a tetra-allylamine salt, tetra-allyloxy ethane, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together.

[0038] As said water-soluble aziridinyl compound, tetramethylolmethane-tree beta-aziridinyl propionate, trimethylol propane-tree beta-aziridinyl propionate, 4, and 4'-bis(ethyleneimine carbonylamino) diphenylmethane etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0039] As said water-soluble polyfunctional epoxy compound, ethylene glycol diglycidyl ether (Pori), propylene glycol (Pori) diglycidyl ether, glycerol (Pori) diglycidyl ether, glycerol triglycidyl ether (Pori), etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together, for example.

[0040] As said silicon system compound, for example 3-(meta) acryloxy methyl trimetoxysilane, 3-(meta) acryloxypropyl dimethoxymethylsilane, 3-(meta) acryloxypropyltrimethoxysilane, 3-(meta) acryloxy propylmethyl dichlorosilane, 3-(meta) acryloxy octadecyl triacetoxysilane, 3-(meta) acryloxy - 2, 5-dimethyl hexyl diacetoxymethylsilane, vinyl dimethyl acetoxysilane, etc. can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together.

[0041] - In loadings-this invention, the loadings of each component of (a) - (e) can be determined enough in consideration of the engine performance as an additive for paper manufacture in the copolymer obtained, and its following range is desirable respectively.

[0042] the sum total molar quantity of the monomer component for which the loadings of the aforementioned (a) component are used -- receiving -- usually -- 97.995 - 55-mol % -- it is 95.99 - 68-mol % preferably.

[0043] the sum total molar quantity of the monomer component for which the loadings of the aforementioned (b) component are used -- receiving -- usually -- 1 - 20-mol % -- it is 2 - 15-mol % preferably.

[0044] the sum total molar quantity of the monomer component for which the loadings of the aforementioned (c) component are used -- receiving -- usually -- 1 - 20-mol % -- it is 2 - 15-mol % preferably.

[0045] the sum total molar quantity of the monomer component for which the loadings of the aforementioned (d) component are used -- receiving -- usually -- 0.005 - five-mol % -- it is 0.01 - two-mol % of within the limits preferably.

[0046] When the loadings of the aforementioned (d) component are less than [0.005 mol %], a paper durability enhancing effect and the filterability effectiveness may become low.

[0047] When the loadings of the aforementioned (d) component exceed five-mol %, the water solubility of the polymer obtained falls, and nonaqueous solubility may be shown, the viscosity of a polymer may rise too much, or it may gel.

[0048] the sum total molar quantity of the monomer component for which the loadings of the aforementioned (e) component are used -- receiving -- usually -- less than [25 mol %] -- it is less than [20 mol %] preferably. When this additive for paper manufacture is used as it is such range, a sufficient paper durability enhancing effect and the sufficient filterability effectiveness can be demonstrated more effectively.

[0049] the polyfunctional (aforementioned f) monomer -- the sum total molar quantity of said monomer -- receiving -- less than [5 mol %] -- it can blend.

[0050] - Composition of the copolymer (an "acrylamide system polymer" can also be called.) in

manufacture-this invention of a copolymer can be conventionally performed by various well-known approaches. For example, so that monomer constituent concentration may become 5 - 30% of the weight in a predetermined reaction container preferably two to 40% of the weight A monomer component, for example, the (a) component, the (b) component, and the (c) component, Or the (a) component, the (b) component, the (c) component, and the (e) component, (d) Prepare a component and the water which is a solvent and a polymerization initiator, for example, a radical polymerization initiator, is added. The need is accepted. Alkyl mercaptan, thioglycolic acid, or its ester Well-known chain transfer agents, such as isopropyl alcohol, allyl alcohol, a metallyl sulfonic acid or its sodium salt, and ammonium salt, can be used suitably, and the acrylamide system polymer in this invention can be obtained by warming under stirring. Of course, the (a) component, the (b) component, the (c) component, the (d) component, and the (e) component can also perform continuation dropping ("continuation addition" can also be called.) etc. according to the description of the component to be used.

[0051] A well-known thing can be used as said polymerization initiator. For example, sodium persulfate, Persulfate, such as potassium persulfate and ammonium persulfate, a hydrogen peroxide, a benzoyl peroxide, Peroxides, such as tert-butyl hydroperoxide and G tert-butyl peroxide, Bromate, such as sodium bromate and a potassium bromate, fault boron acid sodium, Fault boron acid chloride, such as a fault boron acid potassium and fault boron acid ammonium, a fault sodium carbonate, Percarbonate, such as potassium percarbonate and a fault ammonium carbonate, perphosphoric acid sodium, In superphosphate, such as a perphosphoric acid potassium and perphosphoric acid ammonium, and a list, azobisisobutyronitril, Azo compounds, such as a - azobis-2,4-dimethylvaleronitrile, and 2 and 2'-azobis-2-amidinopropane hydrochloride, 2, and 2 '4, 4'-azobis-4-cyano valeric acid and its salt, etc. can be mentioned. In this case, although it can be used even if independent one sort, you may use it combining two or more sorts, and it can also be used as a redox system polymerization initiator combining a reducing agent.

[0052] As said reducing agent, reducing sugars, such as organic amines, such as a sulfite, a hydrogensulfite, N and N, N', and N'-tetramethylethylenediamine, and an aldose, etc. can be mentioned, for example. Moreover, these reducing agents may use one sort independently, and may use it together two or more kinds.

[0053] By the polymerization reaction, the water solution containing the copolymer in this invention can obtain as polymerization reaction generation liquid. After the copolymer in this invention is isolated and refined from the polymerization reaction generation liquid obtained, it can also be used as an additive for paper manufacture with which polymerization reaction generation liquid explains the copolymer later as it is although a proper application can also be presented.

[0054] - The following general formulas (** 3) can show the copolymer in copolymer-this invention.

[0055]

[Formula 3] - Acrylamide monomeric unit p-(anionic vinyl monomeric unit) q-(cationic vinyl monomeric unit) k-(N and N'-bis(meta) (acrylamide alkylene) ureas monomeric unit) j - It is under [said formula] setting. An acrylamide monomeric unit A monomeric unit when acrylamides are included in the principal chain of a polymer by the polymerization is shown. An anionic vinyl monomeric unit A monomeric unit when an anionic vinyl monomer is included in the principal chain of a polymer by the polymerization is shown. A cationic vinyl monomeric unit A monomeric unit when a cationic vinyl monomer is included in the principal chain of a polymer by the polymerization is shown. An N and N'-bis(meta) (acrylamide alkylene) ureas monomeric unit A monomeric unit when N and N'-bis(meta) (acrylamide alkylene) ureas are built into the principal chain of a polymer by the polymerization is shown.

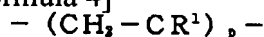
[0056] Among said formula, p shows the repeat number of unit, to a total of 100 of p, q, k, and j, it is usually 97.995-55, q shows the repeat number of unit, and it is usually 1-20, and it is [k shows the repeat number of unit, and it is usually 1-20, and / j shows the repeat number of unit and] usually 0.005-5.

[0057] A copolymer suitable also in the copolymer shown by said general formula has the monomeric unit included in the principal chain of a polymer by carrying out the polymerization of the monomeric

unit [which is shown by the following general formula (** 4) - (** 6 (** 6)) (the 4th class ghost is also included.)] and N, and N'-bis(meta) (acrylamide alkylene) ureas.

[0058]

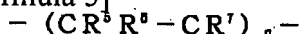
[Formula 4]



However, R1 shows a hydrogen atom or a methyl group among a formula, R2 shows -NR three R4, R3 shows a hydrogen atom or the low-grade alkyl group of carbon numbers 1-8, R4 shows a hydrogen atom or the low-grade alkyl group of carbon numbers 1-8, and even if R3 and R4 are the same, they may be different. p shows the same semantics as the above.

[0059]

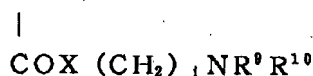
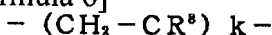
[Formula 5]



However, R5 shows low-grade alkyl groups, such as a hydrogen atom or a methyl group, among a formula, R6 shows a hydrogen atom or -COOH, and R7 shows low-grade alkyl groups, such as a hydrogen atom and a methyl group, or -CH2COOH. Moreover, q shows the same semantics as the above.

[0060]

[Formula 6]



However, R8 shows a hydrogen atom or a methyl group among a formula, R9 shows a hydrogen atom or the low-grade alkyl group of carbon numbers 1-5, R10 shows a hydrogen atom or the low-grade alkyl group of carbon numbers 1-5, and even if R9 and R10 are mutually the same, they may be different. X is O or NH and k shows the same semantics as the above. i shows the integer of 1-5.

[0061] The 4th class ghost of (** 6) is obtained by making the 4th class-ized agents, such as aryl halide, such as alkyl halide, such as methyl chloride and a methyl bromide, benzyl chloride, and a benzyl star's picture, a dimethyl sulfate, a diethyl sulfate, epichlorohydrin, 3-chloro-2-hydroxypropyl trimethylammoniumchloride, and glycidyl trialkyl ammonium chloride, react to the monomer of the above (** 6).

[0062] The monomeric unit included in the principal chain of a polymer cannot be uniquely determined by carrying out the polymerization of the N and N'-bis(meta) (acrylamide alkylene) ureas. It is because two double bonds in which a polymerization is possible to these N and N'-bis(meta) (acrylamide alkylene) ureas exist in intramolecular. The monomeric unit in which one double bond in N and N'-bis(meta) (acrylamide alkylene) ureas carries out a polymerization, and other double bonds remain as a pendant double bond if copolymerization is performed, The monomeric unit which two double bonds in N and N'-bis(meta) (acrylamide alkylene) ureas react, and comes to form an annular solid, Two double bonds in N and N'-bis(meta) (acrylamide alkylene) ureas react. Between two double bonds Or said acrylamide monomeric unit, The monomeric unit between which an anionic vinyl monomeric unit and/or a cationic vinyl monomeric unit come to be placed may generate. Although structure cannot be uniquely determined when N and N'-bis(meta) (acrylamide alkylene) ureas carry out a copolymerization reaction with other monomers, it is included in the copolymer as a certain kind of a monomeric unit. When molecular weight increases compared with the case where N and N'-bis(meta) (acrylamide

alkylene) ureas are not added, it can be checked that N and N'-bis(meta) (acrylamide alkylene) ureas have been incorporated as a monomeric unit into a copolymer.

[0063] The molecular weight of the copolymer in this invention which can be obtained by copolymerizing various kinds of above-mentioned monomers according to the above-mentioned manufacture approach is usually 50,000-10 million.

[0064] - Although the copolymer in the application of a copolymer and additive-this invention for paper manufacture has various applications, if especially used as an additive for paper manufacture, it can demonstrate the property of this copolymer well.

[0065] You may remain as it is. the additive for paper manufacture in this invention -- said polymerization reaction generation liquid -- If needed, other addition components are added and it may be prepared by the copolymer isolated from said polymerization reaction generation liquid. Moreover, it may be prepared by dissolving the copolymer isolated from polymerization reaction generation liquid in water so that it may become predetermined concentration with other addition components added if needed.

[0066] In a suitable mode, the polymerization reaction generation liquid obtained by said polymerization reaction is used as an additive for paper manufacture as it is.

[0067] As solid content concentration, the concentration of the copolymer in the additive for paper manufacture is usually 5 - 40 % of the weight, and is 10 - 30 % of the weight preferably. Moreover, as viscosity of the additive for paper manufacture, it is usually 1,000-100,000cps (measured value in 25 degrees C by the Brookfield rotational viscometer), and is 3,000-20,000cps preferably.

[0068] The additive for paper manufacture of this invention can be added in the wet end section in the production process of paper or the paper board. A sulfuric-acid band may be used or may not be used at all by the class of paper. Moreover, an alkaline substance and the acid are added, and paper making pH may be used, adjusting it suitably.

[0069] For example, in manufacturing paper or the paper board in neutrality thru/or an alkaline field from acidity, all of recycled pulp, such as **, such as **, such as kraft pulp or a sulfite pulp, or unbleached chemical pulp, ground pulp, mechanical pulp, or a thermomechanical pulp, or non-bleached high yield pulp, newspaper used paper, magazine used paper, corrugated paper used paper, or deinking used paper, can be used as a pulp raw material.

[0070] Moreover, as said pulp raw material, mixture with said pulp raw material, asbestos, a polyamide and polyester, polyolefine, etc. can also be used.

[0071] In addition to the additive for paper manufacture concerning this invention, other additives for paper manufacture, such as the acescence of a loading material, a color, the rosin system sizing compound for acid paper making, an alkyl ketene dimer system sizing compound, an alkenyl succinic-acid anhydride system sizing compound, a special denaturation rosin system sizing compound, etc. and neutrality thru/or the sizing compound for alkaline paper making, a desiccation paper durability improver, a humid paper durability improver, a yield improver, a filtration improvement agent, and a defoaming agent, may be added if needed in order to make the physical properties required of each paper type discover. As a loading material, clay, talc, titanium oxide, heavy, or precipitated calcium carbonate can be mentioned, and these may be used by the one-sort independent and may use two or more sorts together.

[0072] The amount of the additive for paper manufacture used concerning this invention to paper manufacture is usually 0.01 - 8 weight section to pulp solid content, and is 0.05 - 2 weight section preferably.

[0073]

[Example] Hereafter, this invention is not restricted by these examples although an example explains the gestalt of operation of this invention. In addition, % is based on weight criteria.

[0074] (Example 1) In the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing 660.620g of water, 269.347g (94.735-mol %) of 50% acrylamide water solutions, Dimethylaminoethyl methacrylate 4.716g (1.5-mol %), 11.203g (1.5-mol %) of 76% methacryloiloxy-ethyl dimethylbenzyl ammoniumchloride water solutions, 0.226g (0.05-mol

%) of 5.204g [of itaconic acids] (2.0-mol %), N, and N'-bis(acrylamide methylene) ureas and 13.596g (0.215-mol %) of 5% sodium methallylsulfonate water solutions were prepared, and the sulfuric-acid water solution adjusted to pH3.0 15%. Subsequently, added 9.13g of ammonium persulfate water solutions 5%, carried out the temperature up to 80 degrees C under nitrogen gas installation, it was made to react for 2 hours, and the copolymer water solution of the solid content of 15.3%, the viscosity (25 degrees C, the Brookfield rotational-viscometer use) of 5,700cps, and pH3.8 was obtained. This was made into the additive A for paper manufacture.

[0075] (Example 2) In the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing 145.655g of water, 47.668g (83.830-mol %) of 50% acrylamide water solutions, Methacrylamide 3.404g (10.0-mol %), 5.679g (4.0-mol %) of 76% acryloyloxyethyl dimethylbenzyl ammoniumchloride water solutions, 0.045g (0.05-mol %) of 1.041g [of itaconic acids] (2.0-mol %), N, and N'-bis(acrylamide methylene) ureas and 1.518g (0.120-mol %) of 5% sodium methallylsulfonate water solutions were prepared. Subsequently, added 1.83g of ammonium persulfate water solutions 5%, carried out the temperature up to 80 degrees C under nitrogen gas installation, it was made to react for 2 hours, and the copolymer water solution of the solid content of 15.7%, the viscosity (25 degrees C, the Brookfield rotational-viscometer use) of 7,200cps, and pH3.8 was obtained. This was made into the additive B for paper manufacture.

[0076] (Example 3) In the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing 689.779g of water, 263.134g (92.55-mol %) of 50% acrylamide water solutions, 28.397g (4.0-mol %) of 76% acryloyloxyethyl dimethylbenzyl ammoniumchloride water solutions, 5.204g (2.0-mol %) of itaconic acids, 1.983g (1.0-mol %) of N,N-dimethylacrylamide, 0.226g (0.05-mol %) of N and N'-bis(acrylamide methylene) ureas and 25.295g (0.40-mol %) of 5% sodium methallylsulfonate water solutions were prepared. Subsequently, added 9.13g of ammonium persulfate water solutions 5%, carried out the temperature up to 80 degrees C under nitrogen gas installation, it was made to react for 2 hours and 15 minutes, and the copolymer water solution of the solid content of 15.2%, the viscosity (25 degrees C, the Brookfield rotational-viscometer use) of 5,400cps, and pH3.7 was obtained. This was made into the additive C for paper manufacture.

[0077] (Example 1 of a comparison) In the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing 642.416g of water, 269.290g (94.715-mol %) of 50% acrylamide water solutions, Dimethylaminoethyl methacrylate 4.716g (1.5-mol %), 11.203g (1.5-mol %) of 76% methacryloyloxy-ethyl dimethylbenzyl ammoniumchloride water solutions, 5.204g (2.0-mol %) of itaconic acids, 15.420g (0.025-mol %) of 0.5% methylenebis acrylamide water solutions, and 16.442g (0.260-mol %) of 5% sodium methallylsulfonate water solutions were prepared. Subsequently, added 9.13g of ammonium persulfate water solutions 5%, carried out the temperature up to 80 degrees C under nitrogen gas installation, it was made to react for 2 hours, and the copolymer water solution of the solid content of 15.3%, the viscosity (25 degrees C, the Brookfield rotational-viscometer use) of 5,070cps, and pH3.7 was obtained. This was made into the additive a for paper manufacture.

[0078] (Example 2 of a comparison) 659.729g [of water], 269.489g [of 50% acrylamide water solutions] (94.785-mol %), and dimethylaminoethyl methacrylate 4.716g (1.5-mol %), 11.203g (1.5-mol %) of 76% methacryloyloxy-ethyl dimethylbenzyl ammoniumchloride water solutions, 5.204g (2.0-mol %) of itaconic acids, and 13.596g (0.215-mol %) of 5% sodium methallylsulfonate water solutions be taught to the 1l. 4 opening flask which attached an agitator, a thermometer, a reflux cooling pipe, and nitrogen gas installation tubing. Subsequently, added 9.13g of ammonium persulfate water solutions 5%, carried out the temperature up to 80 degrees C under nitrogen gas installation, it was made to react for 2 hours, and the copolymer water solution of the solid content of 15.3%, the viscosity (25 degrees C, the Brookfield rotational-viscometer use) of 4,100cps, and pH3.9 was obtained. This was made into the additive b for paper manufacture.

[0079] a presentation and description of the additive for paper manufacture obtained in examples 1-3 and the examples 1-2 of a comparison -- a value is shown in Table 1. the abbreviation used among the table -- AAm:acrylamide MAAm: -- methacrylamide DMAAm:N,N-dimethylacrylamide IA:itaconic-

acid DM:dimethylaminoethyl methacrylate DMBz: -- methacryloiloxy-ethyl dimethylbenzyl ammoniumchloride DABz:acryloyloxyethyl dimethylbenzyl ammoniumchloride MBAAm:methylenebis acrylamide SMAS: -- it is sodium methallylsulfonate.

[0080] In addition, the examples 1 (the additive a for paper manufacture) of a comparison are N of an example 1 (the additive A for paper manufacture), and an example which permuted the N'-bis (acrylamide methylene) urea by methylenebis acrylamide, and the examples 2 (the additive b for paper manufacture) of a comparison are N of the additive A for paper manufacture, and an example which does not contain an N'-bis(acrylamide methylene) urea.

[0081]

[Table 1]

	製紙用 添加剤	組成 (モル%)							性 状		
		(a) 成分	(b)成分		(c) 成分	(d) 成分	(e) 成分	MBAA m	固形分 (%)	粘度 (cps)	PH
			1A	SMAS							
実施例 1	A	AAm 94.735	2.0	0.215	DM 15 DMBz 15	0.05	-	-	153	5700	3.8
実施例 2	B	AAm 83.830 MAAm 10.00	2.0	0.120	DMBz 40	0.05	-	-	15.1	7200	3.8
実施例 3	C	AAm 92.55 DMAAm 1.0	2.0	0.400	DMBz 40	0.05	-	-	152	5400	3.7
比較例 1	a	AAm 94.715	2.0	0.260	DM 15 DMBz 15	-	-	0.025	153	5000	3.7
比較例 2	b	AAm 94.735	2.0	0.215	DM 15 DMBz 15	-	-	-	153	4100	3.9

[0082] (Performance evaluation 1) 1.0% and the pulp slurry which added 3.0% and set pH to 6.0 and 4.5 were prepared for the sulfuric-acid band to pulp to 2.4% of concentration which adjusted corrugated paper used paper to 368ml (it abbreviates to Canadian standard freeness and following C.S.F.) of degrees of beating, the pulp slurry of pH=7.0, and the above-mentioned pulp slurry.

[0083] Subsequently, it diluted with the water of pH=7.0, and 6.0 and 4.5 so that it might become 0.6% about pulp slurry concentration to pulp, each acrylamide system polymer water solution, i.e., the additive for paper manufacture, obtained by each pulp slurry in the above-mentioned example and the example of a comparison, 0.3% and after adding 1.2% and stirring, and filterability was measured. In addition, the appending rate of the above-mentioned chemical is a solid content weight ratio to pulp oven dry weight. A measurement result is shown in Tables 2-4.

[0084]

[Table 2]

	製紙用 添加剤	抄紙 pH	添加率 (%)	DDT (秒)
	無添加	7.0	0	>120
実施例 1	A	7.0	0.3	46.6
実施例 2	B	7.0	0.3	45.0
実施例 3	C	7.0	0.3	37.8
比較例 1	a	7.0	0.3	54.9
比較例 2	b	7.0	0.3	78.0
実施例 1	A	7.0	1.2	98.2
実施例 2	B	7.0	1.2	97.4
実施例 3	C	7.0	1.2	90.5
比較例 1	a	7.0	1.2	119.5
比較例 2	b	7.0	1.2	>120

[0085]

[Table 3]

	製紙用 添加剤	抄紙 pH	添加率 (%)	DDT (秒)
	無添加	6.0	0	91.5
実施例 1	A	6.0	0.3	36.9
実施例 2	B	6.0	0.3	34.2
実施例 3	C	6.0	0.3	32.8
比較例 1	a	6.0	0.3	46.9
比較例 2	b	6.0	0.3	58.3
実施例 1	A	6.0	1.2	33.7
実施例 2	B	6.0	1.2	34.5
実施例 3	C	6.0	1.2	29.0
比較例 1	a	6.0	1.2	42.9
比較例 2	b	6.0	1.2	56.8

[0086]

[Table 4]

	製紙用 添加剤	抄紙 pH	添加率 (%)	DDT (秒)
	無添加	4.5	0	95.0
実施例 1	A	4.5	0.3	46.6
実施例 2	B	4.5	0.3	39.2
実施例 3	C	4.5	0.3	35.3
比較例 1	a	4.5	0.3	50.1
比較例 2	b	4.5	0.3	60.2
実施例 1	A	4.5	1.2	38.8
実施例 2	B	4.5	1.2	37.4
実施例 3	C	4.5	1.2	37.8
比較例 1	a	4.5	1.2	47.9
比較例 2	b	4.5	1.2	64.5

[0087] (Performance evaluation 2) The sulfuric-acid band was added for talc 1.0% to pulp 15.0% to pulp to the pulp slurry of 2.4% of concentration which adjusted BKP (L/N=9/1) to C.S.F.360ml.

[0088] Subsequently, after adding 0.5% to the above-mentioned pulp slurry and stirring to pulp to it, each acrylamide system polymer water solution, i.e., the additive for paper manufacture, obtained in the above-mentioned example and the example of a comparison, pulp slurry concentration was diluted with the water of pH=4.5 so that it might become 0.6%, and filterability was measured. moreover, the pulp slurry which added said additive for paper manufacture for the pulp for paper durability measurement be diluted with the water of pH4.5 so that it might become 0.25% of concentration, paper making be carried out by the sheet machine made from wood, and it be made to dry for 80 seconds at 100 degrees C with a drum dryer, and each measurement be presented with it, noble and after carry out gas conditioning of the handmade paper of obtained basis weight 80 g/m² to the bottom of the condition of 20 degrees C and 65%RH for 24 hours. In addition, the appending rate of the above-mentioned chemical is a solid content weight ratio to pulp oven dry weight. A measurement result is shown in Table 5.

[0089]

[Table 5]

	製紙用 添加剤	抄紙 pH	添加率 (%)	DDT (秒)	比乾燥 破裂強度	張力 (kg/cm)
	無添加	4.5	0.0	60.4	2.22	1.82
実施例 1	A	4.5	0.5	24.1	3.15	3.65
実施例 2	B	4.5	0.5	23.9	3.10	3.70
実施例 3	C	4.5	0.5	21.7	3.12	3.69
比較例 1	a	4.5	0.5	29.2	3.06	3.40
比較例 2	b	4.5	0.5	38.7	3.07	3.30

[0090] (Performance evaluation 3) The sulfuric-acid band was added for white carbon 1.0% to pulp 2.0% to pulp to the pulp slurry which consists of DIP/TMP/BKP=50/40/10 (2.4% of concentration, C.S.F.144ml).

[0091] Subsequently, after adding 0.5% to the above-mentioned pulp slurry and stirring to pulp to it, each acrylamide system polymer water solution, i.e., the additive for paper manufacture, obtained in the

above-mentioned example and the example of a comparison, it diluted with the water of pH=4.5 so that pulp slurry concentration might become 0.6%, and filterability was measured. moreover, the pulp for paper durability measurement diluted with the water of pH=4.5 the pulp slurry which added the additive for paper manufacture so that it might become 0.25% of concentration, paper making be carried out by the sheet machine made from wood, and it be made to dry for 80 seconds at 100 degrees C with a drum dryer, and noble and after carry out gas conditioning of the handmade paper of obtained basis weight 80 g/m² to the bottom of the condition of 20 degrees C and 65%RH for 24 hours, it presented each measurement with it.

[0092] In addition, the appending rate of the above-mentioned chemical is a solid content weight ratio to pulp oven dry weight. A measurement result is shown in Table 6.

[0093]

[Table 6]

	製紙用 添加剤	抄紙 pH	添加率 (%)	DDT (秒)	RDDT (%)	スグトボツン (kgf・cm)	灰分 (%)
	無添加	4.5	0.0	>120	19.0	1.25	2.6
実施例 1	A	4.5	0.5	52.1	43.6	1.90	4.3
実施例 2	B	4.5	0.5	48.0	41.2	1.87	4.4
実施例 3	C	4.5	0.5	44.5	42.3	1.92	4.8
比較例 1	a	4.5	0.5	65.3	39.1	1.82	4.0
比較例 2	b	4.5	0.5	89.2	34.1	1.85	3.9

[0094] Measurement was performed according to the following approach.

a ratio -- bursting strength -- JIS P It measured based on 8112.

SUKOTTO bond -- The internal bond tester (Kumagaya Riki Kogyo K.K. make) was used, and it measured on the adhesive pressure force of 1kg/cm², and the conditions for 30 seconds.

Ash content -- It is JIS except having changed temperature in addition to 550 degrees C. It carried out according to P8128.

DDT -- The same equipment as the 56th volume of the TAPPI journal and the "dynamic DOREINEJJI jar" indicated by the 46th page of No. 10 (1973) is used. A jar with a diameter of 7.5cm is filled with pulp slurry 500ml, a lower cock can be opened, making 600rpm stir, it can be made to be able to filter at the wire gauze of 100 meshes, time amount until the amount of filtrate becomes fixed can be measured, and it can use for filterability evaluation. Here, time amount until the amount of filtrate is set to 200ml was measured.

RDDT -- The same equipment as the TAPPI circuit tester (a jar with a diameter of 7.5cm is filled with a pulp slurry) Paper MEKAZU Improved Hercules which is indicated by the 171st page of a conference (1985) Dynamic DOREINEJJI Air from the lower part so that a mat may not be formed under stirring of 800rpm Delivery, Using the structure filtered at the same time it stops stirring and a supplied air, a jar is filled with pulp slurry 500ml after chemical addition, 50ml of this filtrate is extracted, and the permeability (T. M. (%)) in 620nm is measured. First Pass This T.M. (%) was used as a parameter of a retention. That is, it is shown that filtrate is so transparent that T.M. (%) is high, and it is shown that the yield of a filler and a microfilament is high.

[0095]

[Effect of the Invention] The additive for paper manufacture of this invention can give the outstanding filterability and the outstanding filterability effectiveness, maintaining paper durability equivalent to them as compared with a conventionally well-known polymer, as shown in Tables 2-6.

[Translation done.]